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By

H. H. Power, Barnaby L. Towle, and Joseph B. Plaza

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A METHOD FOR MEASURING HYDRATION-PRESSURE RELATIONSHIPS IN BENTONITIC MATERIALS AVING SHALE

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The benefits of education and of useful knowledge, generally diffused through a community, are essential to the preservation of a free government.

Sam Houston

Cultivated mind is the guardian genius of Democracy, and while guided and controlled by virtue, the noblest attribute of man. It is the only dictator that freemen acknowledge, and the only security which freemen desire.

Mirabeau B. Lamar

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A METHOD FOR MEASURING HYDRATION-PRESSURE RELATIONSHIPS IN BENTONITIC MATERIALS AND HEAVING SHALE

Some shales are thought to heave into the bore hole of drilling wells because of the presence in them of varying quantities of clay materials including the mineral montmorillonite. Such shales expand into the hole when they are wetted by water from the drilling mud. Increases in the apparent volume of the material up to 900 per cent have been recorded.[1] This expanded material is not only capable of filling the hole to a considerable height above point of entry, but it is also able in some cases to exert a pressure of sufficient magnitude to crush the steel casing.

A research program by the authors was conducted at The University of Texas under the general auspices of the Bureau of Engineering Research during the 1940–1941 long session, with the purpose of developing an apparatus and technique for studying hydration-pressure phenomena of bentonitic materials and heaving shale. It was thought that a direct attack on the rate of pressure increase with hydration and the effect of various reagents on retarding such pressure increases would constitute an important addition to the studies previously made on bentonitic suspensions.[2] Accordingly, this paper will be concerned chiefly with a description of the apparatus developed. Subsequent papers will be devoted to data obtained from an investigation of various materials under various physical and chemical environments.

Prior Studies

Kruyt[3] has stated that the process of swelling is distinguished by two features: (a) increase in volume, and (b) pressure of swelling. Increase in volume has been studied extensively for gelatin and similar substances. Loeb[4] performed classical experiments on the relationship of swelling in a gel to pH. Ambrose and Loomis[5] have published similar data for Wyoming Bentonite. Hofmeister,[6, 7] Wo. Ostwald,[8, 9] Spiro,[10] Pauli[11, 12] Fischer,[13] and others have worked on the swelling of gelatin in the presence of electrolytes. Davis and Vacher[14] investigated the effects of electrolytes upon bentonitic gels. The pressure of swelling has likewise been studied widely, but work at the high pressures encountered in the heaving shale problem has been negligible. The following facts have been determined.

Reinke[15] showed that a seaweed (Laminaria) would swell against pressure. The volume increases varied from 330 per cent at 1 atmosphere to 16 per cent at 41.2 atmospheres. Schull's[16] work with dried seeds showed that they withdrew water from a saturated lithium chloride solution having an osmotic pressure of 965 atmospheres. Rodewald[17] discovered that starch swelled against a pressure of 2,500 atmospheres. Graham[18] in 1864 demonstrated that a gelatin film drying on a glass plate often bent or broke it.

Many theories have been advanced to explain the swelling process. One of the earliest of these was that of Procter and Wilson,[19, 20, 21] who applied the Donnan equilibrium explanation to the effect of pH on the swelling of a gel. Katz[22] analyzed the relations between swelling pressure, heat of swelling, relative vapor-pressure, and volume contraction, and presented laws for swelling. Terzaghi[23, 24] has shown the importance of physical factors in the swelling process. His theories conflict in part with those of Katz. Northrop and Kunitz[25, 26, 27, 28, 29, 30] have explained certain aspects of swelling which are not explained by the Donnan condition of equilibrium. They have also been concerned with the swelling pressure of isoelectric gelatin in water. The experiments of Posnjak[31] were concerned with the swelling of raw rubber in organic liquids, and resulted in the following empirical expression for swelling pressure:

$$P = P_o c^k$$

where:

P = swelling pressure
P_o = value of P for $c = 1$
c = concentration of the swelling agent in the gel
k = a constant (3.1 for the system: gelatin + H_2O)

Freundlich[32] and Katz[22] obtained by different means a thermodynamic expression for the swelling pressure:

$$P = -RT/MV_o \ln h$$

where:

P = swelling pressure
R = gas constant
T = absolute temperature
M = molecular weight of the liquid
V_o = specific volume of the liquid
h = relative vapor-pressure of the gel.

The mechanism of swelling in the clay minerals has been investigated with the X-ray by Hofmann, Endell, and Wilm;[33] Hofmann and Bilke;[34] Nagelschmidt;[35] Bradley, Grim, and Clark;[36] and others. They have presented quantitative data on the variation of (001) spacing in a unit cell of montmorillonite with water content. Considerable controversy exists among the various authors on the interpretation of the X-ray data. Bartell and Sims[37] have summarized the theories of swelling advanced prior to 1922.

Design of Apparatus

An examination of the literature failed to disclose an apparatus which would permit the investigation of swelling pressures in the desired range.

However, the system used by Posnjak[31] in his study of the swelling pressure of raw Para rubber in organic liquids was thought to represent the basic idea from which a start could be made.

This device, illustrated schematically by Figure 1, consisted of a porous pot attached to a glass tube by cement in such a manner that the bottom of the pot closed one end of the tube. The other end was closed by a removable cap. A graduated capillary was sealed to the side of the tube and perpendicular to it at a point near the center. Pressure was exerted on the system through the capillary by means of compressed gas from a cylinder. A Bourdon gauge was used to measure the pressure required to prevent swelling of the test material.

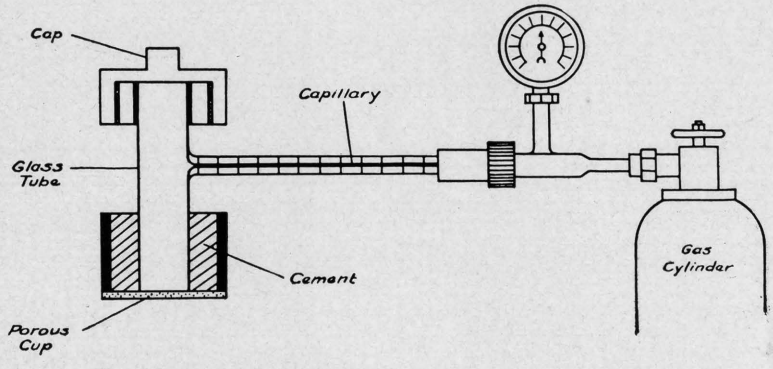

Figure 1. Schematic Drawing of Posnjak's Apparatus (after Kruyt and Van Klooster).

A disc of rubber was placed in the glass tube, where it fell to the porous bottom. The remainder of the tube and part of the capillary were filled with mercury. After replacing the cap on the upper end of the glass tube, the lower end was immersed in a container filled with the desired liquid. Gas from the cylinder was admitted to the capillary to prevent the mercury advancing from its zero position. The pressure required to accomplish this result was shown by the Bourdon gauge.

Posnjak found it impossible to extend his tests above a pressure of approximately seven atmospheres because of the weakness of the porous pot. In addition, constant attendance was necessary to keep the mercury at its proper place in the capillary.

With this background, it was decided to design an apparatus to give results generally comparable to those obtained by Posnjak and yet be capable of working at much higher pressures. The desired working limit was set arbitrarily at approximately 5,000 p.s.i. The porous part of the system was strengthened with partial success by supporting the porous stone disc on a perforated steel disc. Subsequently, it was found impossible to use the stone disc, and a piece of fine screen covered with a porous membrane was substituted for it.

Several attempts were made to design a satisfactory apparatus before an acceptable one was obtained. The first, made of pipe-fittings, sustained a pressure of approximately 150 p.s.i. A porous stone disc covered with a layer of filter paper served to introduce water into the cylinder. (Figure 2.) When the powdered clay was packed into place by hand, the loosely compressed mass did not swell sufficiently to produce a measurable pressure upon wetting with water. Subsequently, a mechanical press was used to compact the clay, and specimens consolidated in this manner were found to be quite satisfactory. The first tests, however, proved that pipe-fittings were inadequate at the pressures obtainable.

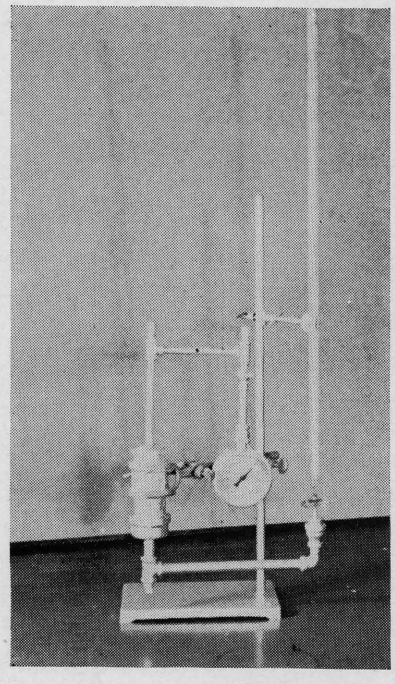

Figure 2. First Apparatus.

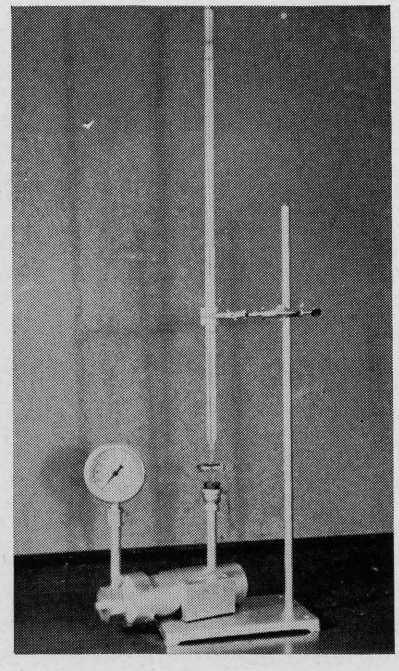

Figure 3. Second Apparatus Using Machined Bomb.

The second attempt resulted in the apparatus illustrated in Figure 3. The cylinder was made from one piece of cold-rolled shafting. The porous stone was supported by a perforated disc which, in turn, was supported by a shoulder machined in the cylinder. By placing the bomb in a horizontal instead of a vertical position, the liquid was given easier access to the porous stone. This reduced the difficulty of removing air bubbles from the system. Asbestos fibre sheets proved to be suitable gasket material. Up to this time all connections to the gauge were made with specially machined heavy pipe nipples. These lacked flexibility and were of necessity rather short. As soon as ⅛-inch O.D. steel tubing of the

kind ordinarily used for such connections was obtained, a new bomb was made with proper seats for use with the tubing. These seats and the mild-steel conical ferrules used with them (Figure 4) are modified versions of those shown in Figure 13 of Worthington's paper on *High Pressure Technique.*[38] They have been used by the authors and others[39] at pressures up to 6,000 p.s.i., and the joints remained tight after alternate connection and disconnection to as many as twenty times. When leaks developed, the ferrule was replaced and the seat smoothed with a small hand reamer.

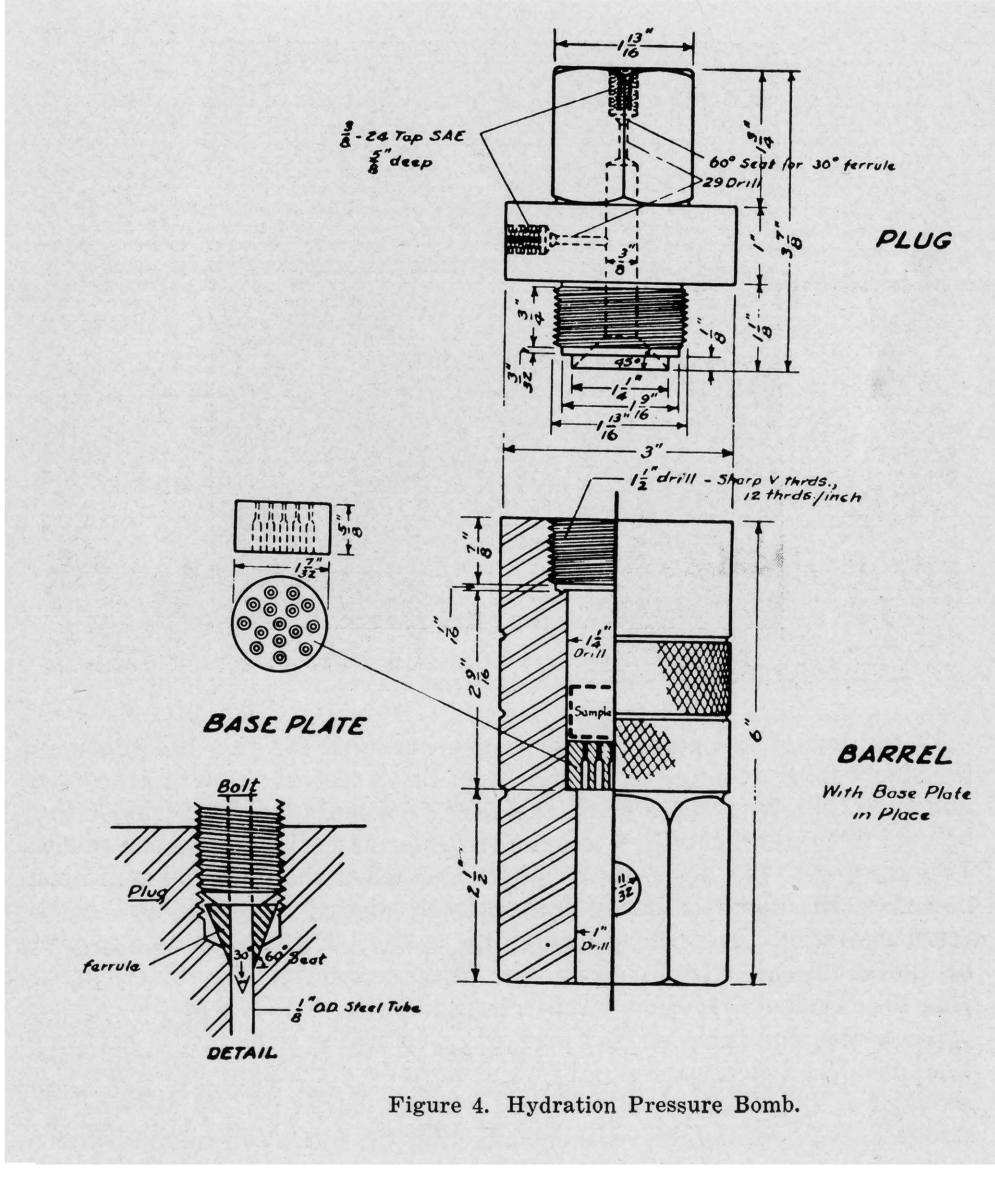

Figure 4. Hydration Pressure Bomb.

The third, and, to date, final design is shown in Figures 4 and 5. It differs from the preceding one only in the manner of connecting the gauge and in the bore of the pressure cylinder. This was decreased from 1¾″ to 1¼″ to allow for a wider gasket. The bomb in its final form consists of a cylinder of cold-rolled steel 3″ O.D. and 1¼″ I.D. The length of the pressure chamber is 1 15/16″ when the apparatus is assembled. One end of the pressure chamber is closed by a heavy steel plug that screws into place. The proper seating of some gaskets requires that they be compressed at pressures of over 60,000 p.s.i.[38] For this reason, it was necessary to make the threads on the plug numerous enough to stand greater pressures than other parts of the apparatus.

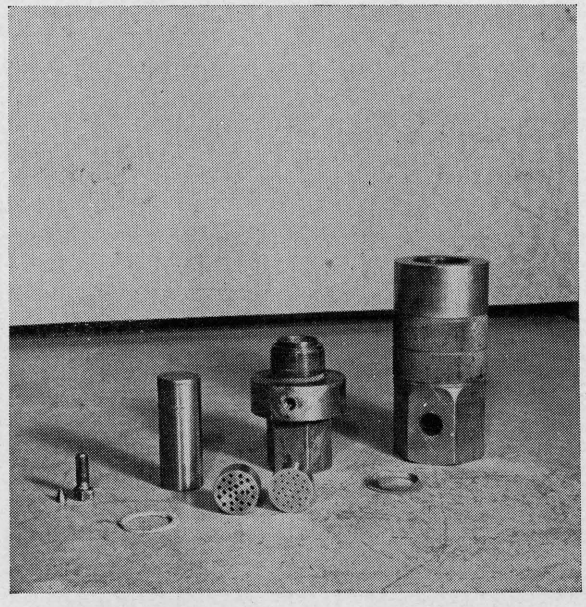

Figure 5. Hydration Pressure Bomb Showing Perforated Disc and Parts.

In the top of the plug, two seats are provided for the attachment of the steel tubing. One of these seats is in the center of the wrench square, and the other is in the side of the plug. Accordingly, the cylinder may be used in connection with a mercury injector as well as a pressure gauge. (Figure 6–a.) The seat which is not used when the gauge alone is connected to the bomb is closed with a steel cone of the same size as the ferrules, but having no hole through the center. The cone is held in place by the usual threaded follower bolt. A hexagonal end is milled on the plug to provide a grip for a wrench in tightening. The end of the cylinder opposite the plug is closed by a steel disc perforated as shown in Figure 4. This disc has a clearance of 1/64″ and rests on a shoulder ⅛″ wide. The shoulder is the weakest point in the cylinder, but it can be widened and strengthened considerably without affecting the operation of the bomb.

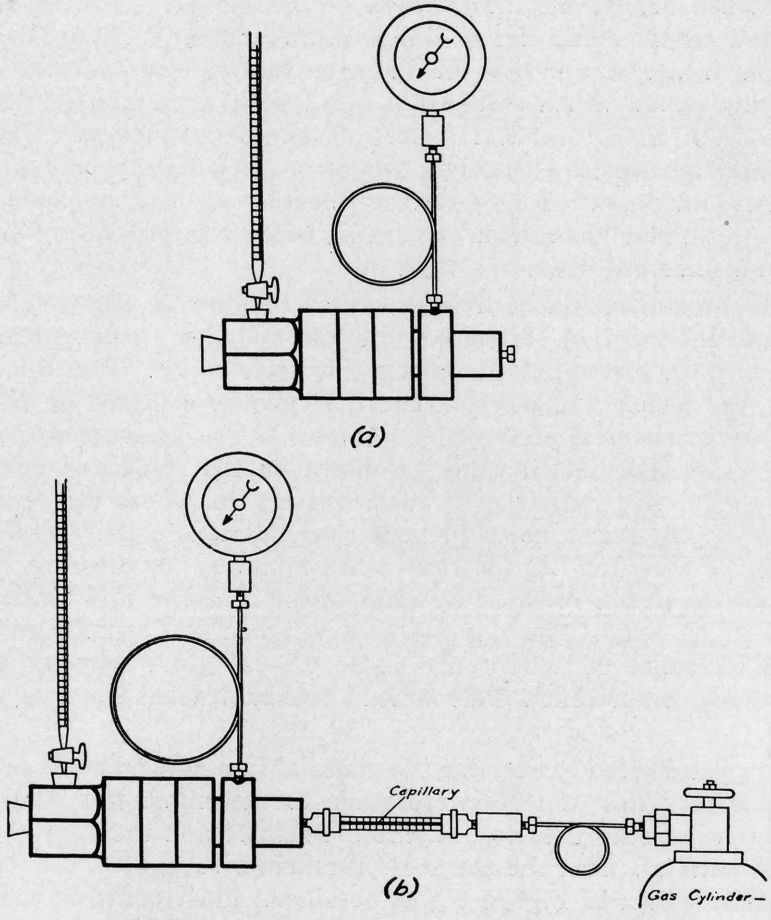

Figure 6. Proposed Modifications of apparatus.
(a) Use of Mercury Pump.
(b) Use of Resistance-Measuring Device.

The reagent chamber is located below the shoulder which supports the base plate. This is simply a 1″ I.D. continuation of the pressure chamber separated from it by the base plate. The end of the reagent chamber opposite the base plate is closed by a rubber stopper. A burette is connected to this chamber so that the amount of liquid withdrawn by the sample can be measured.

Preparing the Apparatus

Since montmorillonite is thought to be partly responsible for the swelling of shales, Wyoming bentonite containing approximately 90 per cent montmorillonite[40] was used in testing the bomb.

The first operation in loading the sample consists of placing the base-plate on the shoulder in the pressure chamber. A porous stone disc was placed on top of the base-plate in the first tests, but it was found that the

stone cracked during the compression of the sample. Wire screen was substituted for the stone disc to eliminate this difficulty. A circular piece of 0-mesh bronze screen 1½″ in diameter was formed over the end of the packing piston which resulted in a flat piece approximately 1¼″ in diameter with a ⅛″ vertical "wall" around its periphery. This was forced into the pressure chamber, where it fitted tightly on top of the base-plate with its raised edge resting smoothly against the walls of the cylinder. A similar piece made of blotting paper was placed on top of the screen and smoothed down to a tight fit.

Next, the air-dried, finely divided powder (Figure 7) was weighed out, and about one-third of it poured into the cylinder. This portion was tamped with the piston before another third was added. With the sample in place, the piston was inserted and the cylinder centered on the platform of the mechanical press. (See Figure 8.) The pressure was quickly brought up to the desired value as shown on the calibrated beam and maintained for five minutes. It was necessary to adjust the press continuously during this time to prevent consolidation in the sample from relieving the pressure. At the end of five minutes, the pressure was released and the piston removed by clamping it in a vise and twisting the cylinder off by hand. The samples used weighed 28.1 grams, and, with a piston clearance of 1/64″ only about 0.2–0.3 gram squeezed by the piston during compression. This amount was subtracted from the sample weight.

Since it was desired to examine the material in a natural state as nearly as possible, a series of tests were made to determine the relationship between the pressure used to compact the sample and the density of the resultant material. Over the range of pressures investigated, the straight-line relation shown in Figure 9 was obtained. Each point on the curve represents the average of two determinations at the pressure shown. The density of air-dried lumps of the material in its natural state was found to be 2.13 grams per cubic centimeter. After the curve of Figure 9 had been prepared, additional samples were compacted at 12,550 p.s.i., which corresponded to the above density on the curve. The average density of these samples was 2.11 grams per cubic centimeter. None differed from the average more than two units in the second decimal place. This average value is surprisingly close to the value predicted by the curve. The density of all samples in subsequent tests was checked by measuring the thickness after compaction and comparing it with that of the samples on which the density was determined. When the same procedure was followed each time in loading and compressing the sample, it was found that the thickness and hence density could be kept within a maximum variation of 2 per cent from the average value.

After the piston was removed, the cylinder was cleaned with an air jet before screwing the plug into place. The pressure cylinder above the sample was filled with mercury. Assuming that the bomb was used with a pressure gauge only, one of the two ferrule seats was closed. It was

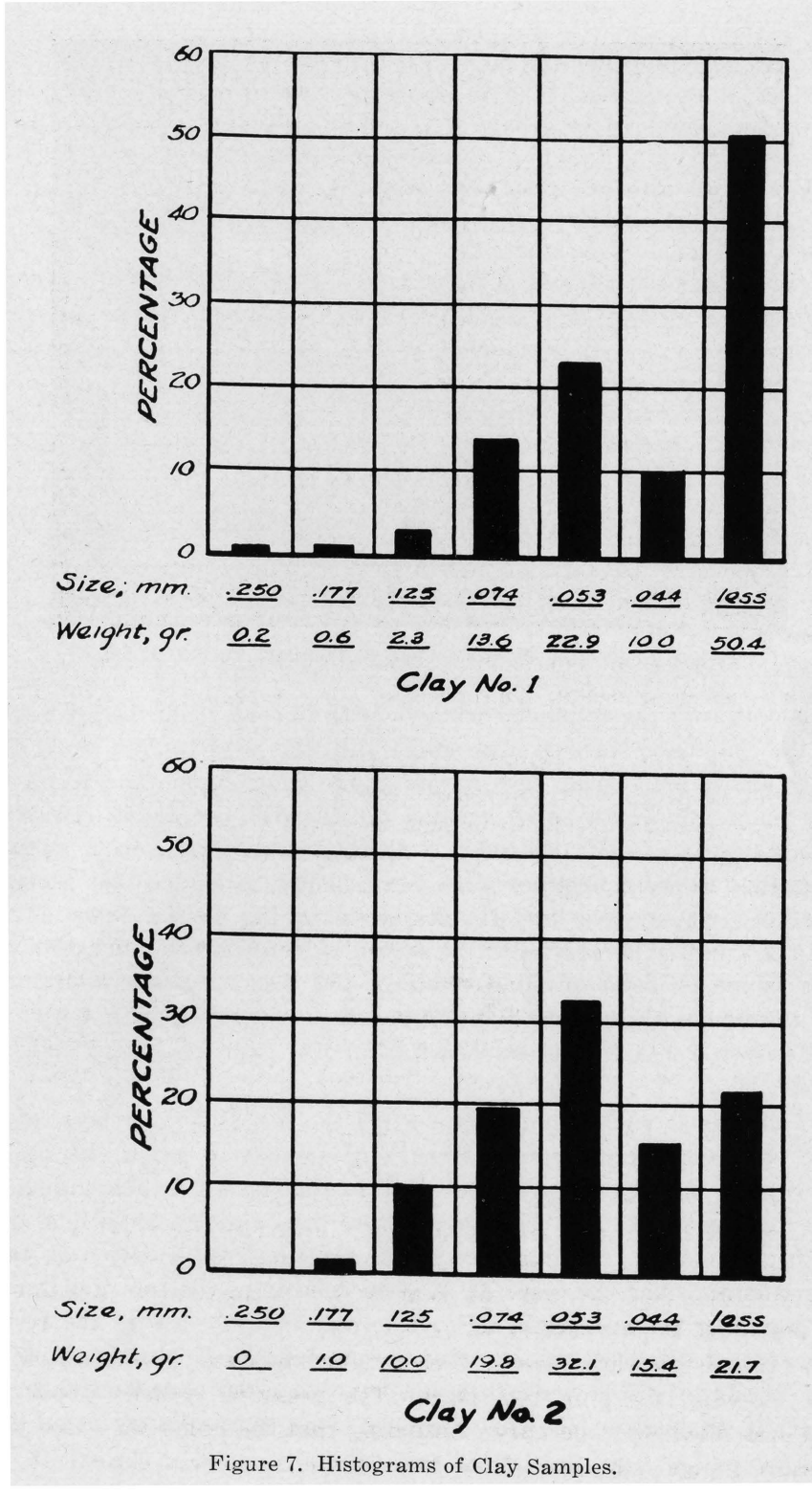

Figure 7. Histograms of Clay Samples.

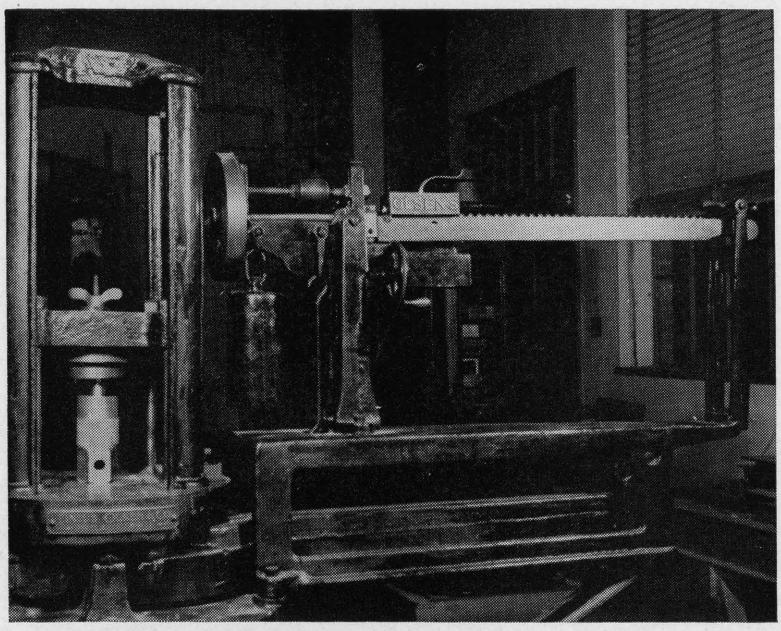

Figure 8. Testing Machine Used to Compact Test Samples.

necessary to rock the cylinder back and forth to remove all the air bubbles from the chamber. Mercury was added until the level surface stood at or slightly above the ferrule seat in the gauge connection. The bomb was placed on its side in a small wooden cradle with the gauge connection pointing upwards. The assembly was then transferred to a constant temperature cabinet, together with the reagent, to insure that temperature of the system was uniform at the beginning of the tests. It was found that the temperature control should be sensitive to a fraction of a degree, since changes of approximately 100 p.s.i. pressure were noted when the bomb was placed in a temperature controlled bath where the variations in room temperature acted on the exposed gauge and connections.

The bomb was rocked once more after the assembly had been placed in the constant temperature cabinet long enough to reach the desired temperature. This procedure made certain that no air bubbles remained in the pressure chamber. The gauge was then connected with a small wrench or pliers, taking due care not to twist off the follower or crush the ferrule and mar the seat. If in good condition, the seat and ferrule were generally pressure tight as soon as the follower forced the ferrule firmly against the seat. When using a new ferrule, it was found necessary to tighten the follower a little harder than usual to make the ferrule conform to the seat. Once this has been done, seating took place more easily.

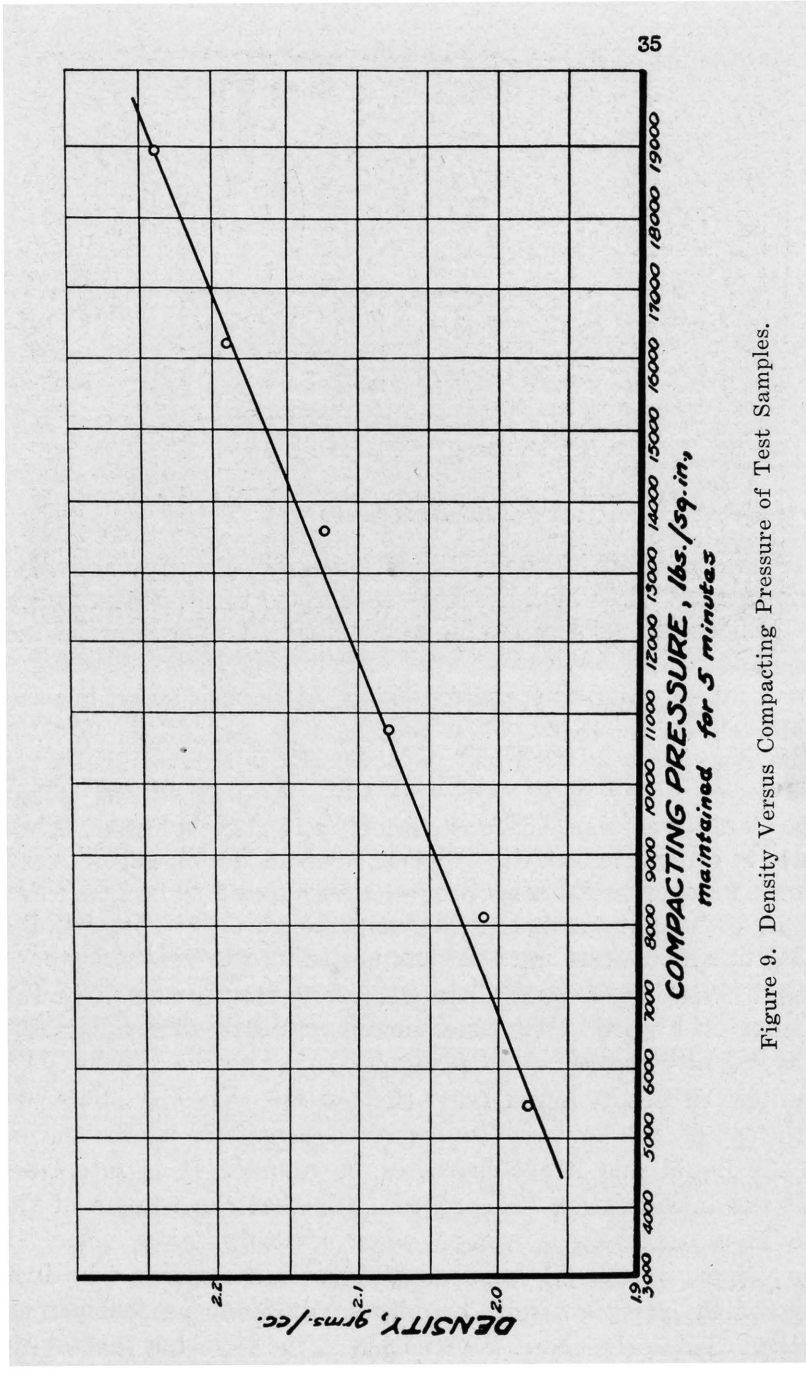

Figure 9. Density Versus Compacting Pressure of Test Samples.

The reagent chamber was prepared by placing one-holed rubber stoppers in the two holes. The tip of a burette was thrust through the smaller stopper and the larger one was connected to a vacuum pump as shown in Figure 10.

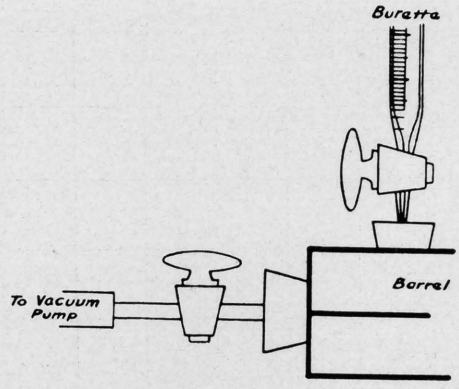

Figure 10. Detail of Reagent Chamber.

Test Procedure

The test was started by evacuating the reagent chamber and then permitting water or other liquids from the burette to fill the chamber suddenly. This method helped to eliminate bubbles trapped in the holes of the base-plate or at other points in the reagent chamber. Since the volume of the reagent chamber was approximately 34 cc., the 50 cc. burette contained approximately 16 cc. when the chamber was filled. The time at which the chamber was filled and the level of the burette finally reached after the bomb filling were recorded. An additional burette filled with the same liquid was placed in the cabinet, and the change of level with time noted in order to check the effects of evaporation on burette readings. The change in level of the control burette was found to be approximately 0.05 cc. per day for water at the test temperature (110° F.). Small corks containing fine holes were used in the burette tops to reduce evaporation.

The final assembly of gauge, burette, bomb, etc., is shown in Figures 11 and 12–a. In Figure 11 the constant temperature cabinet and temperature control is also shown.

As the test proceeds, liquid from the burette wets the blotter at the base of the sample and comes in contact with the sample itself. The sample absorbs the liquid and hence increases in volume. It is interesting to note that the investigation has proved[17, 41, 42] that the volume of the gel plus the liquid actually decreases when swelling takes place. However, the volume of the gel considered alone is increased. The increase in volume of the sample results in pressure increase on the mercury in the chamber. This pressure is transmitted to the Bourdon tube by means of the gauge fluid. Curves obtained with the bomb using Wyoming bentonite will be shown later.

A mercury thermo-regular operating an ordinary electric heater (600 Watt) through a relay switch maintains the proper temperature in the cabinet. The rated sensitivity of the regulator is ± 1/10° C. A large

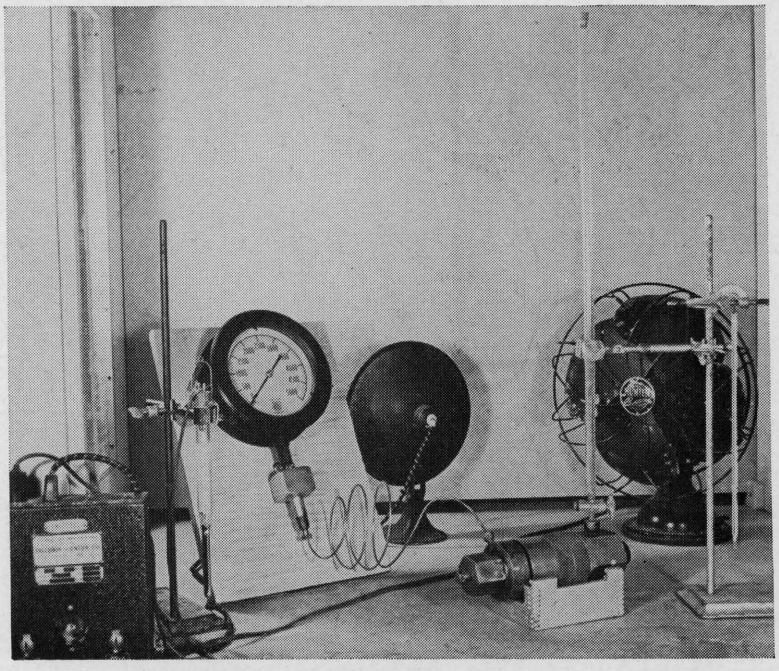

Figure 11. Bomb and Auxiliary Apparatus in Constant Temperature Cabinet.

electric fan keeps the air in the cabinet agitated at all times and causes the temperature to be uniform throughout. This has been checked by placing thermometers at several points in the cabinet. At no time was it possible to detect any difference in temperature between these points. The regulator holds the temperature sufficiently close to the value for which it is set so that no change can be noted on a thermometer graduated to ½ of 1 degree F. The walls, floor, and sides of the cabinet were made of pressed asbestos board ¾″ thick. The front consists of a glassed-in window. Space is available for two and perhaps three bombs and auxiliary equipment.

The gauge used with the assembly (Figure 11) is a No. 1079–D Duragauge made by the Ashcroft American Gauge Division of the Consolidated Ashcroft Hancock Company. The 6-inch dial is graduated every fifty pounds from zero to five thousand p.s.i. The Bourdon tube is alloy steel and the movement stainless steel with welded connections. A zero adjustment is provided, and the manufacturers claim an accuracy of ½ of 1 per cent over the entire scale range.[43] The gauge was calibrated on a Crosby Fluid Pressure Scale (Figure 13), which is capable of measuring pressures from zero to four thousand p.s.i. A vernier on the beam permits reading to the nearest pound. Several re-calibrations were made during the time the gauge was in use. It is customary to use gauges in such work only to one-half of their scale range;[38] but since pressures in this case are applied very gradually with no rapid fluctuations, it is thought that higher pressures may be measured with acceptable accuracy.

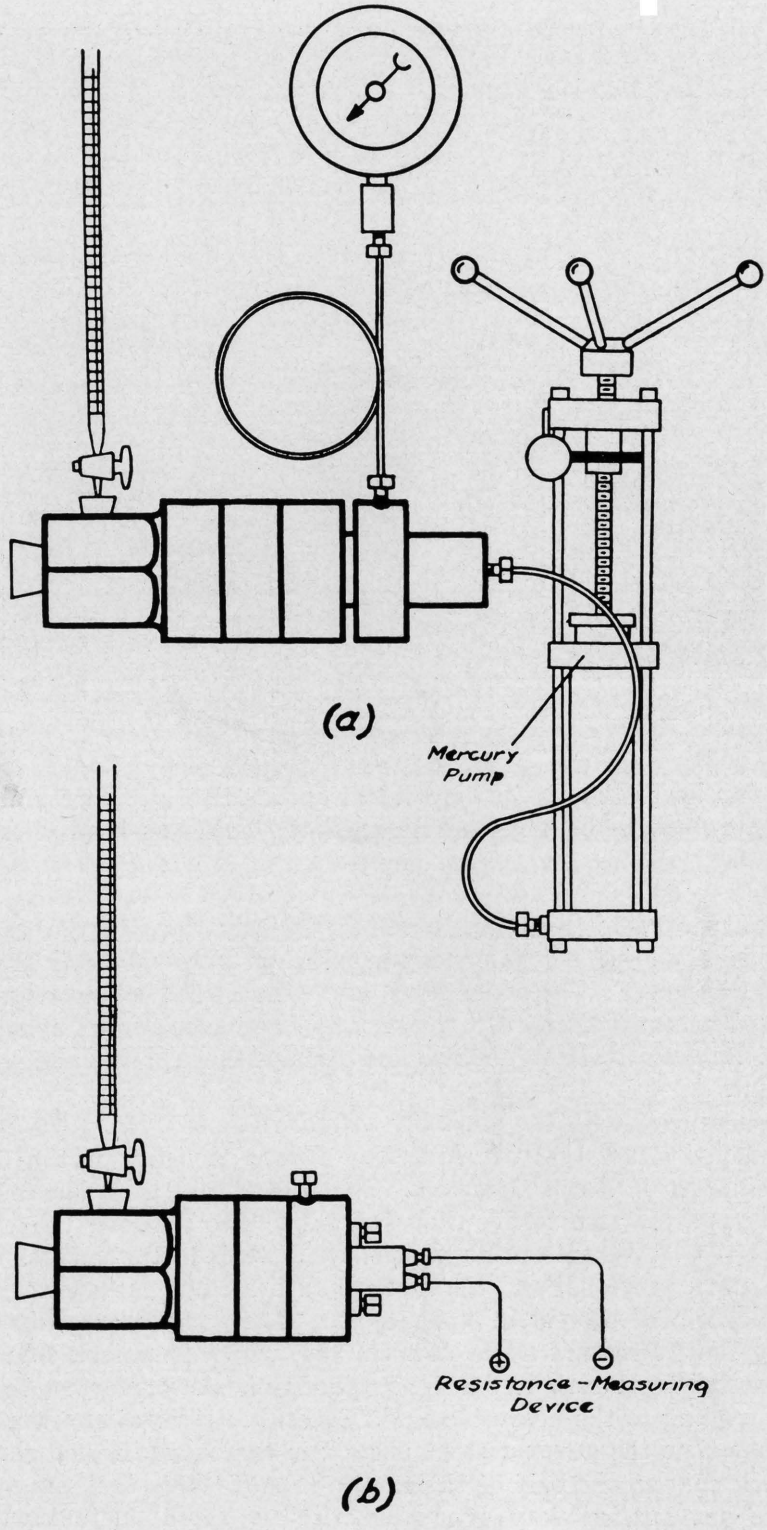

Figure 12. Apparatus as used (a), and Proposed Apparatus (b).

In any case, the accuracy of the gauge was checked several times as the work proceeded.

The gauge and connections were evacuated and filled with oil in order to reduce the expansion of the system as pressure increased. The assembly is shown in Figure 14. The threads of all permanent connections were covered with a paste of litharge and glycerin before being made up.

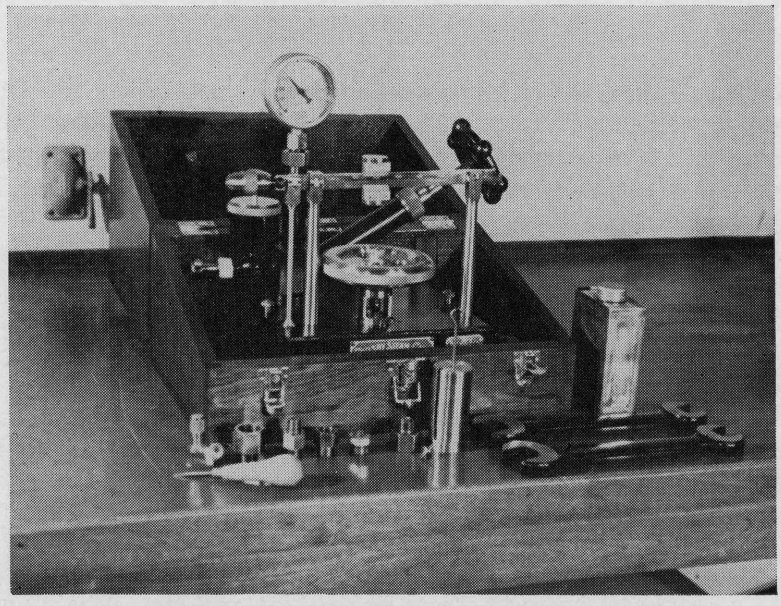

Figure 13. Crosby Fluid Pressure Scale.

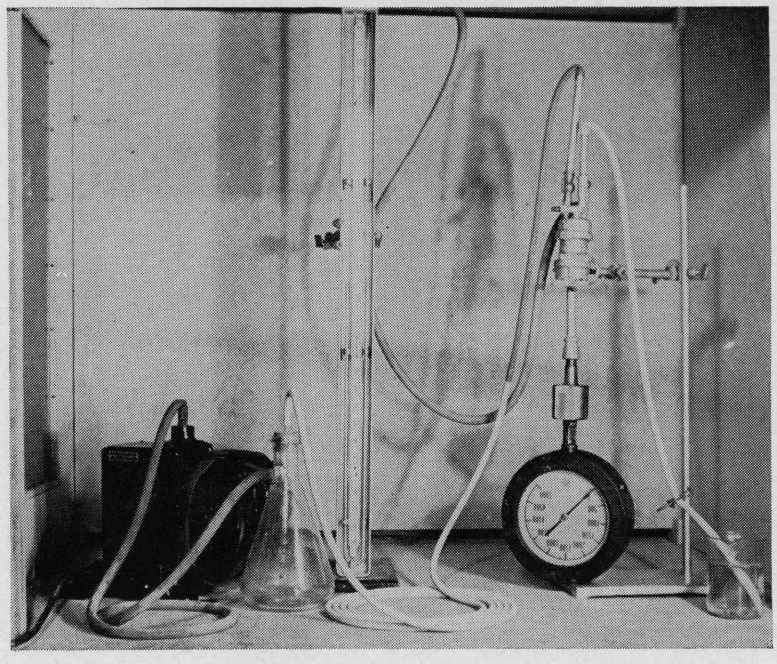

Figure 14. Assembly for Evacuating Air from Gauge.

Tests were run at 110° F., which was conveniently maintained and corresponded to well temperatures at a depth of approximately 2,400 feet in the Gulf Coast. (See Figure 15.) There is nothing significant about this particular depth, but it was found desirable to choose a temperature in the range that might be encountered. The possible variation is shown by the fact that one shale tested came from a depth of somewhat over 8,000 feet and a temperature of 210° F.

Various Methods for Measuring Pressure

Several variations of the means for measuring pressure in the bomb are possible. Each of the variations has certain undesirable features as well as certain advantages. Besides the several possible means for measuring pressure in the bomb, it is also possible to vary the initial condi-

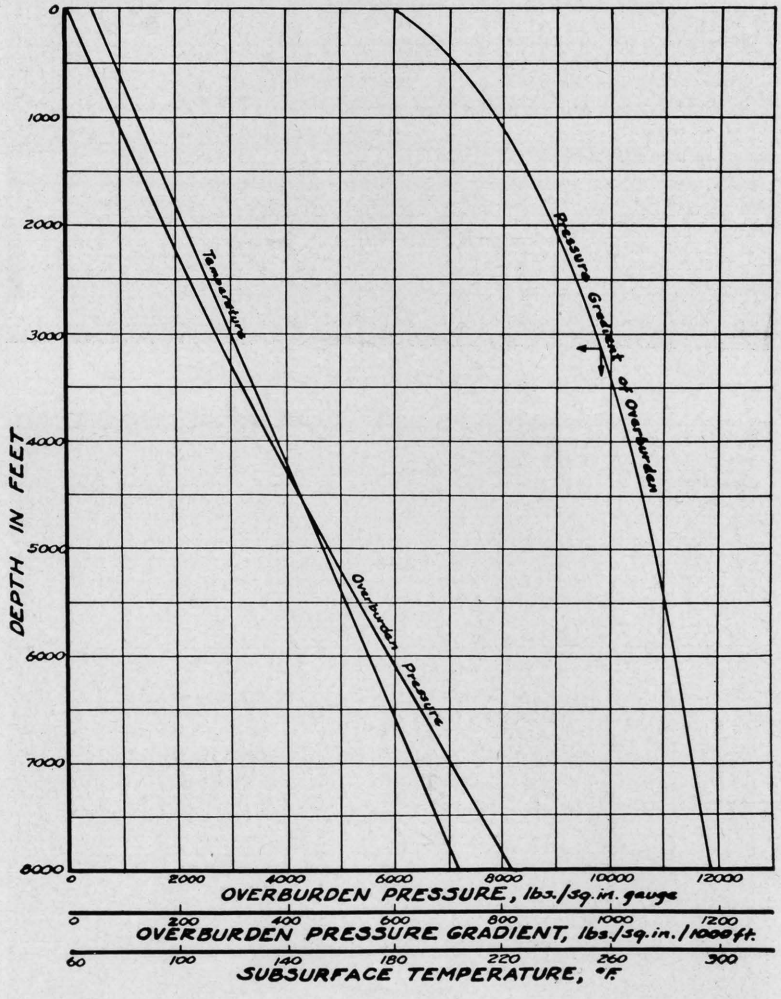

Figure 15. Temperature and Pressure Gradients—Gulf Coast, Texas, Well.

tion of the sample by using material that has already swelled, in order to determine the pressure required to "squeeze out" the liquid. Several suggested uses for the bomb follow.

1. The bomb may be connected directly to a fluid-filled Bourdon gauge in the manner already described. This arrangement is shown in Figure 12–a. It is the only one used to date.

2. The bomb may be connected to a cylinder of compressed gas after the method used by Posnjak[81] and shown in Figures 1 and 12–b. In this case, the pressure necessary to prevent the sample from swelling is measured.

3. A mercury injector and a fluid-filled Bourdon gauge may be connected to the bomb. Liquid may then be forced from a swelled sample somewhat in the manner described by Terzaghi,[23] who, however, used a cylinder and piston apparatus. Figure 6–a illustrates this assembly.

4. Pressure may be measured in the cylinder by means of a resistance gauge such as that described by Bridgman.[44] The bomb in Figure 6–b, which is fitted with the plug shown in Figure 16 illustrates this method.

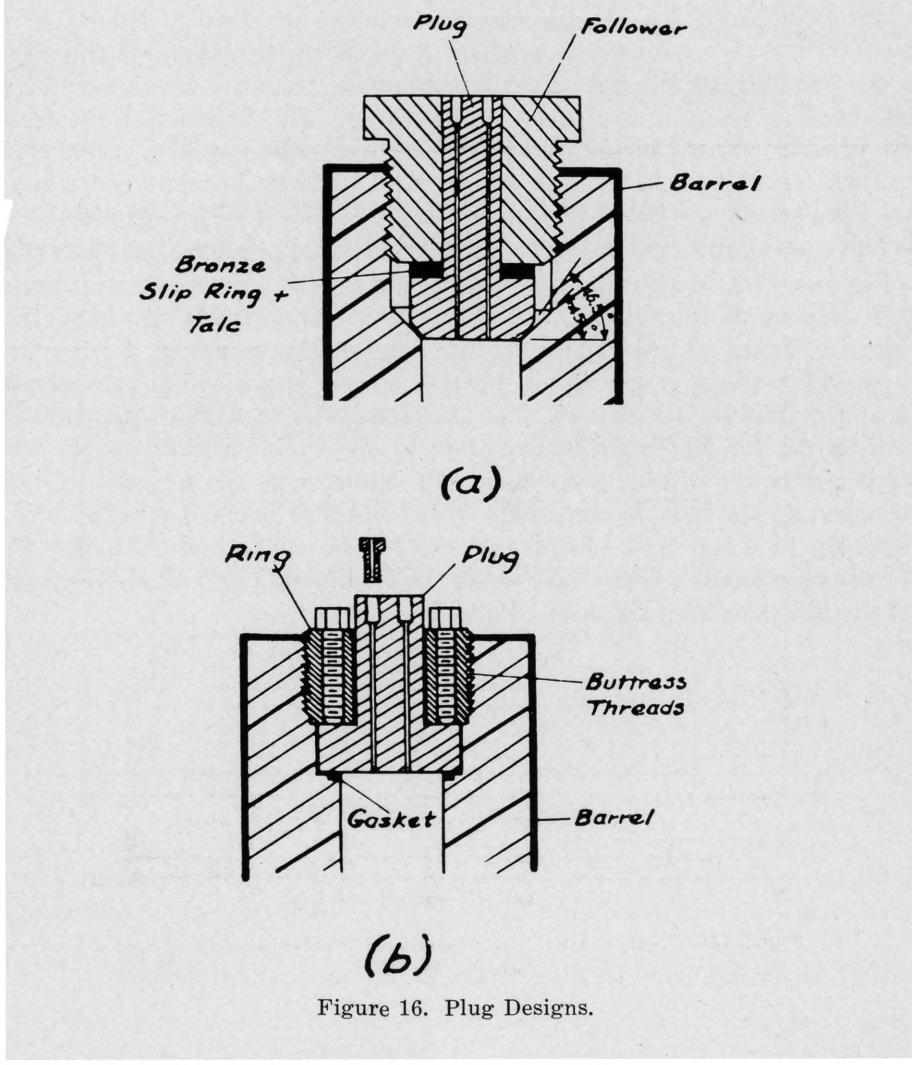

Figure 16. Plug Designs.

The Carey Foster Bridge for measuring the resistance of the coil is not shown.

5. The various reagents that may be used with any of the foregoing methods afford almost endless possibilities for investigation. The swelling properties of many materials may be investigated in addition to those considered herein.

Typical Data

Although a detailed discussion of data obtainable in this investigation will be considered in a later paper, a few pertinent comments and observations may be of significance at this time.

Kruyt[3] pointed out that when a liquid and a gel are compressed together, the increase in pressure favors the process which will produce a decrease in volume, according to the theory of van't Hoff–Le Chatelier. It has been demonstrated[22, 41, 42] that the volume of a swollen gel is less than the sum of the volumes of the gel and the liquid taken separately. Hence, in this case, the process which will produce a decrease in volume of the system is the swelling of the gel. As a consequence, pressure on the liquid and gel together actually increases the swelling. The process of interest in the present apparatus is that which Kruyt calls swelling under "non-uniform" pressure. Here, the pressure of swelling is measured when no pressure exists on the liquid phase of the system. This process is apparently an equilibrium one, in which increasing pressure hinders swelling.

Figures 17 and 18 represent typical curves drawn from data obtained with the bomb illustrated in Figure 12–a. The points at the extreme right in Figure 17 are apparently the equilibrium points in the two tests, as the absorption of the liquid by the sample ceased when the pressure of approximately 1,800 p.s.i. was attained. The maximum pressure was maintained for 24 hours longer than is shown by Figure 18, at which point the bomb was disconnected. No increase in the amount of liquid absorbed by the sample occurred. Other samples reached maximum pressures up to 4,500 p.s.i. Future work will be concerned with the effect of various reagents, other than water, in modifying the hydration-pressure curves illustrated by Figures 17 and 18.

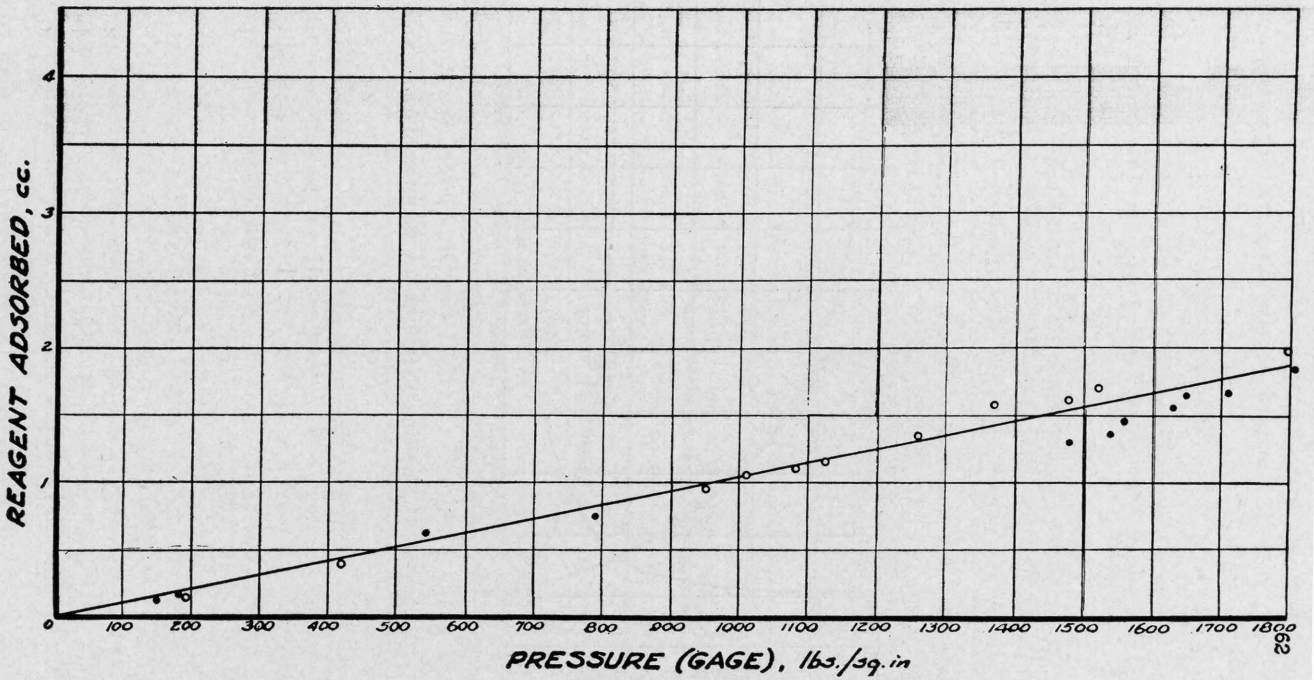

Figure 17. Cc. Reagent Absorbed Versus Pressure. Illustrating Typical Data.

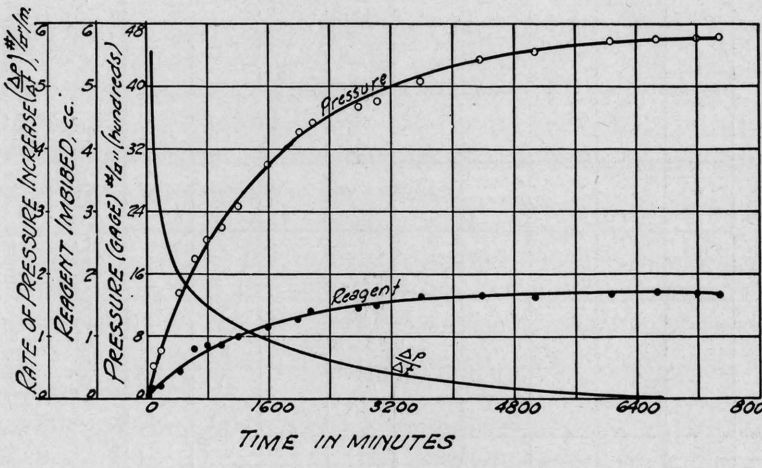

Figure 18. Swelling Relations for Sample No. 1.

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